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1995 Annual Report

RESEARCH AND DEVELOPMENT

**Analytical Laboratory Services
Ontario Ministry of Environment & Energy**

May, 1996

16089

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1995 ANNUAL REPORT

RESEARCH AND DEVELOPMENT

ANALYTICAL LABORATORY SERVICES

MAY, 1996

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Overview

A major direction in MOEE's analytical laboratory services mandate is the continuing evolution away from high-volume, routine testing, and towards core functions and reference centre activities. Accordingly, more emphasis is placed on the analytical methods development activities of the Laboratory Services Branch (LSB). Partnerships also continue to grow in importance, driven by the need to conserve resources and bring a greater range of expertise to the solution of problems.

These changes are reflected in this year's *R&D Annual Report*. A separate section on projects performed by external groups under MOEE funding is not included this year, whereas the section on *Partnerships* is growing steadily. An important aspect of these studies is that the research is focused on providing the tools needed to solve environmental problems or needs. The *LSB Customers* identified under each project provide the driving force for most of the work reported. In studies where internal LSB Units are listed as *Customer*, the principal objectives remain to provide MOEE investigators with the best environmental data possible, at reasonable cost, and with rapid sample turnaround.

For further information on any of the projects described in this report, readers are directed to the Study Leader, or to the Author:

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New Applications of Technology

Introduction

The projects described in this section are ones in which the specific application depends more on the technology used than other aspects of the methodology. The use of sophisticated instrumentation is a common feature of many of these projects, including gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS). Two of the studies described deal with the use of a technique used in sample preparation - called solid-phase extraction (SPE). With the use of SPE techniques it is possible in some applications to not only achieve more rapid analyses, but to virtually eliminate the use of toxic solvents previously used for sample extraction. For example, SPE methods have been reported in which 100-200 mL of solvent have been replaced by 5-10 mL. Ongoing development in this area is expected as different SPE products become available commercially.

Another new project described in this section applies synthetic organic chemistry to analytical problems - by manufacturing new compounds with specific molecular structures that can be used to complex with sample components and thus provide an effective means of sample cleanup. To date, such sophisticated cleanup methods have not been used in routine sample preparation procedures. Another aspect of this work is the preparation of analytical standards of analytes for which commercial standards are not yet available.

Overall, the projects described in this section illustrate that the term "new technologies" can encompass a wide range of activities - not just those that are based on sophisticated instrumentation. Regardless of the technology investigated, the goals of this work remain to provide our customers with improved analytical services, such as lower detection limits, greater specificity, faster turnaround, and reduced cost.

I. Negative Ion Chemical Ionization (NICI) Confirmation of Halogenated Organics

| | |
|---------------|---|
| Study Leader: | Vince Taguchi |
| Study Team: | Don Robinson (retired), Kim Ngo, Bob Kleins |
| Customer: | LSB, MOEE, external agencies |

Objective

To improve Branch capability to identify unknown organic compounds.

Background

Electron capture negative ion mass spectrometry (ECNIMS), a subset of NICI, is a technique used to identify halogenated organics at detection limits comparable to electron capture detection (ECD). ECD detection limits for halogenated organics are lower than flame ionization detection (FID) or electron ionization (EI) mass spectrometry. Sample extracts analyzed by GC/MS usually employ EI ionization. EI cannot be used to identify halogenated organics analyzed by ECD unless the sample extracts are concentrated. This is not always practical or possible. Hence a mass spectrometric technique that can accommodate the same extract that was used for the ECD analysis is extremely useful. There is some variation in the ECNIMS spectra because of instrument design; however, for most organics ECNIMS spectra that are very close to spectra published in the scientific literature (Stemmler and Hites) can be obtained. For some compounds, there will be significant differences.

Results

An ECNIMS library with 90 entries was originally set up on the Finnigan 4500s mass spectrometer. The Finnigan 4500s have now been retired and all ECNIMS work has been transferred to the VG Trio-2 mass spectrometer. Because ECNIMS spectra are instrument-dependent, a new library with 78 entries has been set up on the Trio-2. Confirmations of toxaphenes and PCBs have been done in fish extracts.

Current Status

This work has been completed except for further additions to the ECNIMS library. This is an on-going process. A method that covers chemical ionization techniques (CI and NICI) has been written and approved (E3335B). The product code for these analyses is GCMS3335.

A quantitative method for halogenated organics can be set up if requested and justified. In the case of the toxaphenes, several methods of quantitation have been used by different researchers, and as yet there is no universal agreement on which method of quantitation is the best.

II. Solid Phase Extraction (SPE) GC/MS Analysis of PAH in Drinking Waters

| | |
|---------------|--------------------------------------|
| Study Leader: | Patrick Crozier |
| Study Team: | Larry Matchuk |
| Customer: | All Drinking/Surface Water Customers |

Objectives

To develop a solid phase extraction GC/MS-based method for the trace level determination of polynuclear aromatic hydrocarbons (PAH) in drinking waters, surface waters and groundwaters which will provide high quality data with faster analysis time, increased analytical capacity and a reduction in the use of hazardous chemicals.

Background

Polynuclear aromatic hydrocarbons (PAH) are ubiquitous environmental pollutants. Several PAH have been found to have carcinogenic properties eliciting their inclusion in environmental control legislation. The World Health Organization (WHO) has recommended the concentration of six representative PAH (fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)pyrene and indeno(1,2,3-c,d)perylene) not to collectively exceed 200 ng/L in drinking waters. The Ontario Ministry of Environment and Energy has established the maximum acceptable

concentration (MAC) for benzo(a)pyrene in drinking waters to be 10 ng/L (Ontario Drinking Water Objectives - Revised 1994).

The Drinking Water Analyses Section determines PAH by using a liquid/liquid extraction/HPLC/Fluorescence method. Sample preparation is by batch processing with external quality control (QC) measures. Although the HPLC method is reliable (CAEAL accredited), it possesses several less than ideal qualities. Its major drawbacks are the use of large quantities of hazardous solvents (extraction solvent and HPLC mobile phase), low column resolving power, restricted linear range, front end interferences with highly coloured samples and the need to confirm positive results by mass spectrometry. The development and use of solid phase extraction GC/MS methodology eliminates most of the problems associated with the current HPLC testing method as well as permits the monitoring of individual sample processing performance through the use of labelled surrogates and internal standards.

Results

A routine SPE GC/MS method has been developed to test for 17 PAH target compounds. The wet chemical preparation procedure requires 800 mL of sample and consists of sample acidification (pH = 2), surrogate (d_{12} -chrysene) addition, sample aspiration through C₁₈ SPE cartridges, cartridge air drying, toluene (4 mL) elution and extract evaporation (final volume = 0.5 mL). After the addition of an internal standard (d_{10} -phenanthrene) instrumental analysis is completed. Compound separations are accomplished using a 30m x 0.25mm x 0.25um DB-5ms column and a 35 minute double ramp oven program. A six segmented single ion monitoring (SIM) program is used to identify (retention time plus target ions), quantify (parent ion) and confirm (ion ratios) target compounds. Minor method changes may be required to fine-tune the method for trace level (low ng/L) PAH testing.

| PAH SPE GC/MS Method - Instrument and Method Performance | | | | | | | | |
|--|---|------|----------------|------|------------|------|---------------------------------------|------|
| Target Compound | Instrument Performance (500 pg/uL, n=10) | | | | | | Method Performance (100 ng/L, n=9) | |
| | Retention Time | | Quantification | | Ion Ratio | | Recovery (%) | %RSD |
| | Result (min) | %RSD | Result (%) | %RSD | Result (%) | %RSD | | |
| phenanthrene | 10.08 | 0.01 | 102 | 3 | 23 | 1 | 98 | 5 |
| anthracene | 10.20 | 0.02 | 101 | 4 | 22 | 1 | 95 | 5 |
| fluoranthene | 12.99 | 0.01 | 102 | 3 | 19 | 1 | 97 | 6 |

| | | | | | | | | |
|---------------------------|-------|------|-----|---|----|---|----|----|
| pyrene | 13.35 | 0.01 | 102 | 4 | 20 | 1 | 93 | 6 |
| benzo(a)anthracene | 16.57 | 0.01 | 104 | 3 | 26 | 1 | 82 | 7 |
| chrysene | 16.65 | 0.01 | 103 | 3 | 28 | 1 | 86 | 7 |
| dimethylbenz(a)anthracene | 19.10 | 0.01 | 102 | 3 | 63 | 1 | 76 | 9 |
| benzo(b)fluoranthene | 19.10 | 0.01 | 106 | 3 | 22 | 1 | 88 | 6 |
| benzo(k)fluoranthene | 19.16 | 0.01 | 104 | 3 | 21 | 1 | 87 | 7 |
| benzo(e)pyrene | 19.71 | 0.01 | 105 | 3 | 29 | 1 | 82 | 7 |
| benzo(a)pyrene | 19.84 | 0.01 | 106 | 3 | 22 | 1 | 77 | 9 |
| perylene | 20.02 | 0.01 | 105 | 3 | 26 | 1 | 86 | 10 |
| indeno(123-cd)pyrene | 22.93 | 0.01 | 108 | 3 | 20 | 1 | 81 | 12 |
| dibenzo(ah)anthracene | 23.05 | 0.01 | 109 | 4 | 24 | 1 | 69 | 10 |
| benzo(b)chrysene | 23.38 | 0.02 | 100 | 4 | 24 | 3 | 72 | 10 |
| benzo(ghi)perylene | 23.79 | 0.01 | 94 | 4 | 20 | 3 | 74 | 11 |
| coronene | 30.80 | 0.02 | 93 | 5 | 45 | 8 | 81 | 18 |

Current Status

The wet chemical preparation (solid phase extraction) and instrumental analysis portions of the SPE GC/MS method have been established. The SPE GC/MS method is being compared to the current liquid/liquid extraction HPLC/Fluorescence method. Method validation is in progress using NIST reference standards, Canadian Association for Environmental Analytical Laboratories (CAEAL) performance audit samples and low level naturally contaminated surface waters.

Publications and Presentations

1. Polynuclear Aromatic Hydrocarbon (PAH) SPE GC/MSD Analysis Method - Research and Development Progress Report June 19, 1995 : LSB-DWA Internal Report by P. Crozier and L. Matchuk

III. LC-MS of Environmental Samples

| | |
|---------------|---|
| Study Leader: | Vince Taguchi |
| Study Team: | (a) Particle Beam: Kim Ngo, Dave Wang (b) Electrospray: Steve Jenkins, Dave Wang |
| Customer: | Mass Spectrometry Unit |

Objectives

To expand Branch capabilities for the determination of thermally-labile organic compounds and to identify unknown organic compounds.

Background

The premier instrumental technique for the detection and quantitation of trace organic pollutants is gas chromatography-mass spectrometry (GC/MS). Unfortunately, many compounds cannot be determined by GC/MS because they are thermally labile, are very polar, or have a very high molecular weight. The relatively new technique of liquid chromatography/mass spectrometry (LC/MS) is applicable to such compounds. As LC/MS is in an early stage of development for environmental applications, much research is still required before these methods can be called "routine".

Several LC/MS techniques have been reported in the scientific literature. At the Laboratory Services Branch, the use of both Particle Beam and Electrospray LC/MS have been examined.

Results

(a) Particle Beam LC/MS. N-nitrosodiphenylamine (NDPhA) has been extracted from water samples with Ambersorb 572. NDPhA was extracted from the Ambersorb 572 with dichloromethane:toluene and the extract was evaporated to dryness in a tapered silanized glass vial. The overall recovery was approximately 25%. Because narrow bore LC columns (2 mm i.d. x 25 cm) must be used with the particle beam interface, the NDPhA must be reconstituted in the starting mobile phase. Otherwise, peak splitting will occur. NDPhA and its thermal degradation product

diphenylamine (DPhA) are separated chromatographically on either reverse phase or normal phase systems. Detection limits for NDDPhA by normal phase liquid chromatography/ultra violet detector (LC/UV) were approximately 1 ppb. NDDPhA decomposes to (DPhA) when it contacts a hot ion source. This is not a problem because of the available retention time data. Detection limits by LC/MS were highly variable. Therefore, the current method consists of detection by LC/UV with confirmation by MS. A draft method is being prepared.

Preliminary work has been done on carbamates and pesticides currently being done by LC/UV by the Pesticides/Herbicides Unit. A feasibility study was done to see if these methods could be done by LC/UV/MS. Additional sample preparation was found to be necessary. The extracts had to be concentrated, evaporated to dryness and reconstituted in the starting mobile phase. Confirmations by LC/MS are possible but detection limits are highly variable.

Characterizations by LC/MS have been done by normal phase and reverse phase chromatography. Because of the limited chromatographic resolution of LC columns, fractionation of the extracts is mandatory. A draft method has been written.

(b) Electrospray LC/MS. Preliminary work has been done on the analyses of Diquat, Paraquat and Glyphosate by electrospray LC/MS. This work has been set up on a VG ZAB-EQ hybrid mass spectrometer. With this system, high resolution and hybrid MS/MS capabilities can be used in conjunction with electrospray. Electrospray LC/MS has been demonstrated to be functional on this instrumental system. Currently hybrid MS/MS is being investigated to improve the analytical signal-to-noise. Hybrid MS/MS capabilities can be used to identify unknowns by EI, CI, electrospray and other ionization techniques.

Current Status

Electrospray LC/MS gives significantly better detection limits than Particle Beam, and therefore is better suited for most Ministry applications. Particle Beam LC/MS has the advantage of giving mass spectra that more closely resemble standard electron ionization spectra, therefore Particle Beam LC/MS is still valuable for compound identification applications. Work is continuing on both techniques, with the emphasis on electrospray applications.

IV. Clean-up Methods for Analytes in Oil-Contaminated Samples; Preparation of Organic Standards

| | |
|---------------|--------------------------------|
| Study Leader: | Michael Tjepkema |
| Study Team: | Otto Meresz |
| Customer: | Analytical Laboratory Services |

Objectives

To develop rapid, rugged and cost-effective clean-up methods for extracts from heavily oil-contaminated samples; to synthesize new analytical calibration standards.

Background

There is a need for a rapid, efficient and simple procedure for the separation of analytes from hydrocarbon (eg. waste oil) matrices. Presently, analytes are separated from hydrocarbon material using time consuming chromatography using Florisil. Often even this method is unsuccessful.

It has been known for some time that urea **1** and thiourea **2** form 'inclusion' complexes with straight chain paraffins and branched chain paraffins, respectively. The complexion is the result of the urea forming a tunnel-like complex with the paraffin molecule and complexion is closely related to the size and shape of the hydrocarbon. Certain unsaturated hydrocarbons also form these complexes depending on the degree of unsaturation relative to the chain length of the saturated portion of the molecule. It is thus possible in principle to add a saturated solution of urea/thiourea in methanol to the waste sample in hexane such that the paraffinic material is complexed and precipitated, while the analytes (due to their different shapes) remain in the hexane layer.

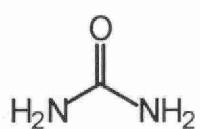
Results

A large number of 'model' hydrocarbon urea/thiourea complexes have been

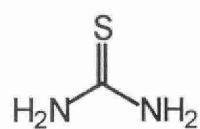
prepared to investigate the scope and limitations of this method. By using a model mixture of straight chain saturated paraffins and straight chain unsaturated paraffins containing aromatic compounds in hexanes, treatment with urea/methanol succeeded in removing essentially all the paraffinic material while the aromatic material remained untouched and gave good recoveries. Further work with urea inclusion complexes has been postponed as the more immediate Ministry need arose in connection with current analytical problems in laboratory development work.

The analysis of industrial wastes entering the Grand River Basin requires special standards and surrogates preferably as labelled compounds which are not commercially available. As the MOEE does not have an ongoing program of organic chemical synthesis, and such contract work has been very expensive in the past, we have undertaken the synthesis of a number of the required organic compounds. The synthesis of labelled compounds can be quite complicated because only compounds with simple structures are available in the deuterated form.

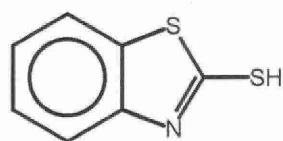
When carrying out the synthesis of a labelled compound, the chemical reactions are first investigated and optimized with unlabelled material. Currently 2-meccaptobenzothiazole **3** and its corresponding disulphide **4** have been prepared with unlabelled materials and the synthesis of the labelled compounds **5** and **6** is in progress. In addition to the preparation of the disulphide **4** the redox relationship between the mercaptan and the disulphide had to be clarified for practical analytical purposes. In addition, a number of requests have been received for other synthetic work for more deuterated analytes (eg. carboxin-d₅ **7**) and also for special mass markers (eg. decacyclene sulphonic acid **8**) for liquid chromatography/mass spectroscopy mass calibrations.



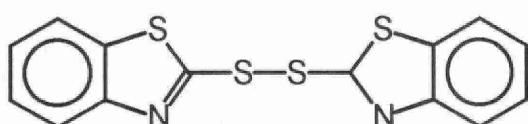
urea (1)



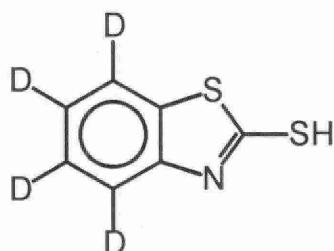
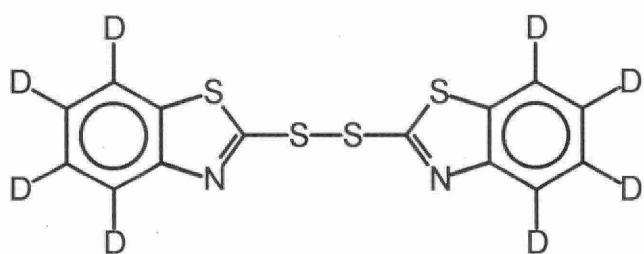
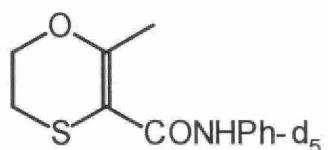
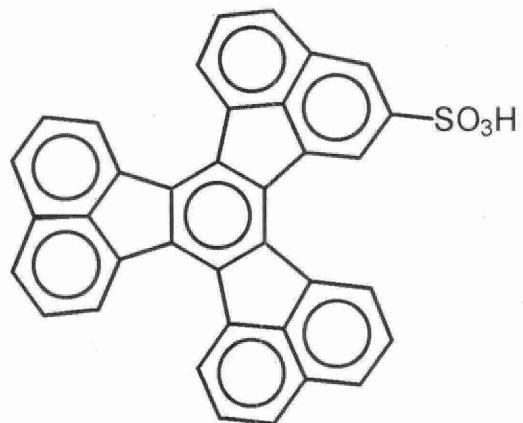
thiourea (2)



2-mercaptopbenzothiazole (3)



2-mercaptopbenzothiazole (4)

2-mercaptopbenzothiazole-d₄ (5)2-mercaptopbenzothiazoledisulphide-d₈ (6)carboxin-d₅ (7)

decacyclene (8)

V. Solid Phase Extraction Cartridges for Dioxin/Furan Cleanup

| | |
|---------------|----------------------------|
| Study Leader: | Kathy Taylor |
| Study Team: | Tereza Gobran, Eric Reiner |
| Customer: | Dioxin/Furan Unit |

Objectives

To reduce cost and time associated with dioxin sample cleanup without compromising the quality of the final product.

Background

A SPE-based procedure reported in the literature by Chang et al was examined. The project was started in 1993. At that time soil was examined and further work was needed. During 1994 several soil experiments were repeated. There were problems achieving acceptable recoveries and removing high levels of chlorinated diphenyl ethers (DPEs) from the soil samples. A manifold system capable of running 16 columns at a time was purchased.

Results

During 1995, water(MISA), air, soil and sediment samples were cleaned up using this method. Water and air samples were successful. Problems were encountered with soil and sediment samples. Modifications of the manifold were pursued and advances will be made with respect to these more difficult matrices.

Current Status

As part of a project funded by MOEE (ERP 729C), the use of SPE for dioxin sample cleanup is being examined. Continuation of this work by the Laboratory Services Branch depends on the success of ERP 729C.

Methods Development

Introduction

A greater degree of effort was spent in this activity area in 1995, compared to previous years. The wide range of projects reported deal with improvements in quality control, sample preparation, and instrumental analysis. Both organic and inorganic analytes were investigated, with the majority of the methods based on analyses performed by GC/MS (organics) or ICP/MS (inorganics) instrumentation.

Many of the projects in this section were initiated as a direct result of Ministry customer requests to expand analytical capabilities in certain areas - usually to add a new analyte to a routine monitoring list, to lower method detection limits, or to broaden the range of sample types analyzed for an existing analyte. In some cases, projects were initiated internally to improve the ruggedness and throughput of an existing method, or to achieve improved quality control. The ongoing mission to lower analytical costs and provide more rapid reporting of results are often prime motivators for internally-initiated projects.

For any environmental analytical laboratory, minor method improvements are made on a continuous basis. In some cases, the improvements are small enough so that a major change in the method description is not required. The descriptions provided here are only for those projects which require significant changes to the method description, or even a completely new method write-up.

I. Expansion of Drinking Water Analyses Capabilities

| | |
|---------------|---|
| Study Leader: | Ram Sadana |
| Study Team: | Lorna Grey, Jadwiga Mazur |
| Customer: | Environmental Monitoring and Reporting Branch |

Objectives

To develop routine analytical methods to test for additional organic target compounds in drinking water.

Background

The Ontario Ministry of Environment and Energy (MOEE) revised its Ontario Drinking Water Objectives (MOEE:ISBN # 0-7743-8985-0) in 1994. The new organic target compounds included in the Ontario Drinking Water Objectives were expanded to 50 semi-volatile organic pesticides/ industrial chemicals. LSB to date did not have analytical testing methods for 8 of these target chemicals. The following is the listing of the compounds with testing methods currently under development:

Semi- Volatile Organic Compounds not on LSB Drinking Water Analyses Target Compounds List

| | | |
|------------|-----------------------------|-----------|
| Aldicarb | Bendiocarb | Triallate |
| Diquat | Paraquat | Dinoseb |
| Glyphosate | Nitrilotriacetic acid (NTA) | - |

Current Status

The Pesticides/ Herbicides Unit of the DWA Section is expanding its HPLC-UV method for the Carbamates (LSB Method E3158A) to include the five carbamates (aldicarb, bendiocarb, triallate, aldicarb sulphone and aldicarb sulphoxide) in the existing method. Developmental work is underway to determine their resolution, detection limit, extraction efficiency, and low-level detection criteria (W and T). The completion of the R & D work is targeted for July, 1996.

Dinoseb is being added to the present chlorophenol/ phenoxyacids herbicides method (LSB Method E3119A). Preliminary developmental work indicate no major modification will be required to the existing method. The completion of developmental work is targetted for September, 1996.

Ion chromatography equipment was purchased in order to develop a method for the analysis of Nitrilotriacetic acid (NTA). The completion of this project is anticipated in December, 1996.

The Mass Spectrometry Unit is working on developing analytical methods for diquat, paraquat and glyphosate, based on using liquid chromatography/mass spectrometry (LC/MS) technology.

II. Hexane Micro-extraction Roller Methodology

| | |
|---------------|------------------------------------|
| Study Leader: | Eva Duchoslav |
| Study Team: | Jadwiga Mazur |
| Customer: | All Drinking/Surface Water Clients |

Objective

To develop a micro-extraction method for chlorinated organic pesticides and PCBs in drinking water samples.

Background

Micro-extraction techniques offer several advantages over traditional liquid/liquid extraction techniques. The reduction in the use of solvent cuts down the amount of hazardous wastes produced and the cost involved. The simplicity also eliminates the need for sample clean-up which is time-consuming as well as a source of analyte loss and experimental error. The sample preparation time can be reduced from days to hours. Extraction can be carried out in the sample container, which removes the need for glassware preparation. The solvent micro-extraction method has been applied to the analysis of a list of pesticides by the U.S. Environmental Protection Agency (USEPA Methods 505). In 1994, the extension of method 505 to the analysis of all organochlorine compounds targeted in method OWOC-E3120B, was the objective of the RAC Project No. PDF12.

A new method for the analysis of chlorinated organic pesticides/PCBs has been proposed to replace an existing analytical method (LSB Method E3120B). Evaluation of the method using naturally contaminated waters and fortified real matrix samples suggested inconsistent yields of several target compounds.

Results

The hexane roller/micro-extraction method was tested on a variety of real matrix spikes and naturally contaminated groundwaters. Modifications to the sample preparation procedure to improve method performance for PCBs and other compounds such as Mirex and octachlorostyrene have been examined. Increasing the ionic strength of the solution with NaCl was found to have an adverse effect on the extraction selectivity for chlorinated waters. With the elimination of salting out and the use of 1,3,5-Tribromobenzene as an internal standard, the hexane roller/micro-extraction provides a rugged sample preparation technique for the determination of OCs/PCBs. The recoveries of 36 target compounds are above 80%. The within-run precision is in the range of 2-5%. The detection limits of the current method can be easily met. Sample preparation time is reduced by four times, from two days for 12 samples to 4 hours for 12 samples. Also, with the proposed method, Toxaphene can be determined at 50ng/L.

With the exception of PCBs, the recoveries of all compounds were statistically comparable to recoveries obtained with a traditional liquid/liquid extraction. The inconsistent results for PCBs are enhanced with the higher degree of PCB chlorination.

Alternative approaches to improve recovery of PCBs worsen the yield of some of the other 36 target compounds.

Current Status

Full method validation has been completed. The method write-up/bench procedure has been started. A separate project to verify sample storage protocol has been initiated.

III. Addition of Dioxin Like PCBs to Dioxin/Furan Analysis

| | |
|---------------|---|
| Study Leader: | Dave Waddell |
| Study Team: | Karen MacPherson, Kathy Taylor, Terry Kolic |
| Customer: | All Customers of Dioxin/Furan Unit |

Objectives

To analyze for the dioxin-like PCB congeners (PCBs #77,105,118,126 and 169) in a variety of sample types. The analysis will give an estimate of the toxic equivalent component contributed by PCBs to the total 2,3,7,8-TCDD toxic equivalents (TEQs) for any one sample.

Background

Other units within the Laboratory Services Branch are presently monitoring these PCB congeners, but due to their toxicity the selectivity and low detection limits achievable by using a High Resolution Mass Spectrometric isotope dilution method is required.

Results

Literature searches have been conducted and materials reviewed. Calibration standards have been taken through through a preliminary verification. Final verification of the standards still requires some work.

Instrument experimental conditions were modified to accomodate characteristic ion masses of the PCB congeners for analysis by using selected ion monitoring. Dioxin Unit cleanup methods were tested for PCB recoveries. More work needs to be done in this area in order to optimize the cleanup procedures.

Current Status

The PCB/Dioxin provisional method can be used for the analysis of real samples, but the determination of precision and accuracy, and the completion of the validation studies for various sample types, must still be performed.

IV. Determination of N-Nitrosodimethylamine (NDMA) in Air using Ambersorb Tubes

| | |
|---------------|---|
| Study Leader: | Steve Jenkins |
| Study Team: | Vince Taguchi, J-P. Palmentier |
| Customer: | LSB, MOEE (Regional Offices), external agencies |

Objective

To provide a simple, rapid method for the determination of NDMA in air.

Background

Air samples have been analyzed for NDMA by the TAGA 6000 Mobile Monitoring Unit and by the Mass Spectrometry Unit. The latter laboratory used impingers containing high purity water. After a known volume of air was passed through the water, the water was extracted with dichloromethane and the extract was analyzed by gas chromatography-high resolution mass spectrometry (GC/HRMS). This method was subsequently modified. The NDMA is extracted from water using a granular adsorbent, Ambersorb 572, and is isolated by filtration. The adsorbent is air-dried and transferred to an autosampler vial. The NDMA is extracted from the Ambersorb with a small volume of dichloromethane in the autosampler vial.

This study was designed to see if the impinger step could be eliminated. The air sample was drawn through a sorbent tube containing Ambersorb 572. The adsorbent was extracted with dichloromethane and the extract was concentrated and analyzed by GC-HRMS.

Results

Air tubes were packed with Ambersorb 572 in 3 layers with glass wool between the layers. This allowed us to check for breakthrough in the second and third layers. The packed air tube was spiked with the internal standard, d₆-NDMA, on the first layer. Studies with d₆-NDMA alone showed that there was very little breakthrough to the second layer. Two sets of air tubes were sent out for field tests. Results from these 2 sets were comparable to results from the TAGA 6000.

Current Status

Parallel studies between the Ambersorb air tubes and the TAGA 6000 have to be done to validate the method.

V. The Stability of Trifluralin in Organic Solutions

| | |
|---------------|----------------------------|
| Study Leader: | Eva Duchoslav |
| Study Team: | Jadwiga Mazur |
| Customer: | Pesticides/Herbicides Unit |

Objectives

To obtain shelf-life data and to determine storage conditions for Trifluralin extracts and expiration dates for Trifluralin standard solutions.

Background

The Ontario Drinking Water Objective has been established for Trifluralin (2,6-dinitro-N,N-dipropyl- α,α,α -trifluoro-p-toluidine) at 45 µg/L. Trifluralin was added to the current LSB method for the determination of chlorinated pesticides (OCs/PCBs; LSB method E3120B) in March 1994.

The Trifluralin internal quality control data demonstrated high bias in 1994. Also, the final report from the RAC Project No.PDF12 suggests that Trifluralin is not stable in the iso-octane solution used in the OC/PCB method. Several literature references document that Trifluralin is not stable when exposed to light.

Results

The stability of Trifluralin in acetone, iso-octane and hexane under different storage conditions has been studied. It was found that the rate of decomposition of Trifluralin in hexane and iso-octane under laboratory conditions is approximately 20% in a month. The loss of Trifluralin is due to exposure to light. Reactions with other chlorinated pesticides present in the solution were not found to contribute to the loss. No decomposition was observed in case of Trifluralin in acetone.

When protected from light, Trifluralin in iso-octane or hexane maintained its integrity. The shelf life for solutions stored in this manner was verified to be six months.

Modification to the existing analytical protocol will improve precision and accuracy for the determination of Trifluralin.

Current Status

The project is complete. Recommendations will be incorporated in the OWOC-E3120B method and as well as its new version, hexane roller micro-extraction method.

VI. Determination of Total Tin in Drinking Water by ICP-MS

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|---------------|---|
| Study Leader: | Mark Powell |
| Study Team: | Lian Liu, Ray McVicars |
| Customer: | Environmental Monitoring and Reporting Branch |

Objective

To develop a method to measure total tin in standing pipe drinking water and to find a correlation between the amount of tin leached from the lead/tin solder.

Background

Previously, there have been concentrations of lead exceeding the drinking water guidelines in many areas of Ontario. In most cases the source of contamination was not from the water treatment plant process or the private well, but from the solder used to connect the pipes in the distribution system. The purpose of this study is to establish a relationship between lead and tin used in the soldering process of pipes and how concentration data may be used to determine this. In order to determine tin concentrations in drinking water, a method has been developed using ICP-MS.

Results

An analytical method has been developed using the technique of ICP-MS for the determination of total tin in drinking water. The detection limit is 0.05 ug/l.

Current Status

The method has been used to evaluate tin concentrations in standing pipes from a total of 150 houses in southern and central Ontario. The method has been incorporated into the LIMS system and the method documentation is in the process of being approved.

VII. Determination of Total Iodine in Drinking Water

| | |
|---------------|---|
| Study Leader: | Mark Powell |
| Study Team: | Ray McVicars |
| Customer: | Water Technology Branch (A. [Tony] Edmonds) |

Objective

To develop a method to measure the concentration of total iodine in treated drinking water.

Background

Water distribution systems (mains) have a limited life. Most systems become clogged with deposits made by bacterial action before corrosion has affected the mechanical integrity of the pipes. Maintenance of chlorine residuals and mechanical cleaning can help but in many cases this is either not possible or too late and pipe

replacement becomes the only alternative. Many systems in Ontario are approaching the end of their useful life of 70 or more years. Replacement costs for Ontario are estimated at \$600,000,000 per year to keep pace with the need.

A potential technology, which has been used successfully elsewhere, is water main cleaning using chlorine/iodine disinfectant. Provided the iodine is at low enough concentrations so it does not present a significant hazard to anyone consuming the water, it appears to work effectively. This low iodine/chlorine cleaning process is to be piloted in Ontario at Port McNicoll this year and this will be the source of the samples for analysis. Should the cleaning process be effective there will be widespread future demand for total iodine analysis from many municipalities across Ontario.

Results

Total iodine in aqueous solutions (drinking water) can be determined by ICP-MS as I^+ which will be a proportional representation of I_2 . Iodine is a halogen and will produce mostly negative ions upon ionization. However, some positive ions are produced which can be measured by our mass spectrometer. Although a smaller number of positive ions are produced, this will not adversely affect the detection limits achievable by using ICP/MS.

The ion source completely ionizes the atoms and molecules, and hence, total iodine will be measured. It does not matter which form or valence state iodine is in (iodide or iodate), as long as there is minimal particulate in the sample. Excessive particulate may give rise to adsorption or complexing of iodine onto the surface of the particulate and cause a bias in the true concentration measurements. Detection limits, precision, accuracy and potential interferences are in the process of being determined.

Current Status

The detection capability required must approach 1 ng/l. It is not yet known what the confidence level of the analytical results will be. This will very much depend on the measurement of reference materials, detection capability and method precision. As the customer is emphasizing reproducibility rather than accuracy, a semi-quantitative method approach is followed. If we are successful in developing a pre-treatment to stabilize concentration variation from the time the sample is taken in the field until the time of analysis, development of a semi-quantitative method is possible.

VIII. Analysis of Mercury in Drinking Water by ICP-MS

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|---------------|-------------------------------|
| Study Leader: | Mark Powell |
| Study Team: | Ray McVicars, Russell Bennett |
| Customer: | LSB Spectroscopy Unit |

Objective

To adapt the ICP-MS based Drinking Water Surveillance Program (DWSP) method to include mercury as an analyte to be measured simultaneously with the 23 other DWSP elements to enhance "turn around" time and reduce costs.

Background

The analysis of mercury in drinking water is an important parameter in Ontario's DWSP program. It is presently measured by cold vapour atomic absorption spectrophotometry. ICP-MS determines 23 other elements simultaneously for the DWSP program and it would be of an advantage in terms of cost savings to add mercury to this workstation. This investigation will study a new technique to minimize the "memory effects" on mercury caused by the sample introduction system of the ICP-MS.

This technique involves the addition of gold (at low concentrations) as an internal standard. The gold forms an amalgam with mercury causing a reduction in the memory effects caused by the conventional sample introduction system by minimizing mercury adsorption on the walls of the introduction system.

Results

Initial results are encouraging. A detection limit was established at 0.1 ppb. Without the gold internal standard, the "washout" time between standards of 100 ppb mercury was 8 minutes. With the gold added, the washout time was reduced to 3 minutes. Without gold addition, standardization was erratic due to wall adsorption on

the sample introduction system. Slope and intercept drift was prevalent. The slope and intercept drift was substantially reduced with the addition of a gold internal standard.

Current Status

The ICP-MS method is not yet ready to replace existing methods for mercury analysis. Detection limits have to be improved by at least a factor of 5 and more experimentation must be conducted to characterize the effects of the gold internal standard on washout time. When a "rugged" method is devised for mercury as an individual parameter measurement, it will be added to the DWSP ICP-MS method. Additional experimentation must be conducted at this stage to ensure confidence.

IX. Development of Alternative Methods for Testing Hazardous Waste Leachate

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|---------------|---------------------------|
| Study Leader: | Heng Jin |
| Study Team: | Yvonne Jones, Rusty Moody |
| Customer: | Waste Management Branch |

Objective

To develop a rapid, rugged, accurate, and precise leach test for organics in hazardous waste; to be used in support of Regulation 347.

Background

The Ontario Regulation 347 leachate extraction procedure was developed for inorganic analytes and some pesticides and herbicides. The need to develop land disposal restrictions for hazardous wastes and to expand the list of leachate toxic

chemicals required a leach test that is applicable to a wide range of organics, including volatiles. The USEPA has developed such a method, which employs a zero headspace extractor to prevent the loss of volatile organics. However, this method is costly and prone to equipment breakdown.

Results

In an evaluation of the USEPA method for volatiles, average recoveries ranged from 82 to 120%. Bromoform was not detected. For the establishment of standard curves and recovery determination, methanol is used to spike standards into water samples. For reliable analytical results, it was found that the volume of methanol added should be as little as possible, and never greater than $1.3 \mu\text{L}$ per mL of liquid sample. In a study of sample storage times, it was determined that samples should be analyzed no longer than three days after extraction, when the recoveries of some analytes were observed to have dropped to 40% of their initial concentrations.

Current Status

The semi- and non-volatile parameters to be studied and their proposed regulatory levels in the waste filtrate are currently under discussion with staff of the Program Development Branch. Experiments will be conducted to evaluate the suitability and reliability of bottle extraction for the extractable analytes by referring to the USEPA method. Analytical methods will be developed for target analytes in the waste filtrate at the proposed regulatory levels.

X. Determination of Hg in Water, Industrial Wastes and Sludges by Flow Injection AAS

| | |
|----------------|-------------------------------|
| Study Leader : | Pamela Wee |
| Study Team : | Darryl Russell, Audry Stewart |
| Customer : | CSMM Section |

Objective

To bring on-line a flow injection mercury system (FIMS) to supplement conventional methods using continuous flow analysis (CFA). The FIMS is almost four times faster than the CFA system.

Background

Both methods are based on cold vapour AAS but differ in how reagents and testing materials are delivered for reaction. Operating conditions for the FIMS had to be fine-tuned in order to provide analytical results that are comparable to those obtained by CFA.

Results

The FIMS methods for sewage and waters appear to serve as viable supplemental methods for CFA. Detection capabilities are similar; the FIMS is less prone to sample carryover, but is less tolerant to inexact matrix matching of oxidants in standards and samples.

Current Status

Further testing is required to determine ruggedness of the FIMS and to verify comparability of analytical results. The method requires documentation and internal audit for LSB approval. More testing needs to be done on sludges.

Partnerships

Introduction

In the past year, partnerships have allowed LSB staff to share unique resources and expertise with others to evaluate new technologies and instrumentation for improving the measurement of contaminants in the environment. Partnerships with analytical instrument companies, for example, were used for studies on Supercritical Fluid Extraction (SFE), Accelerated Solvent Extraction (ASE), Quadrupole Ion Trap mass spectrometry, and High Performance Liquid Chromatography-Direct Insertion Nebulizer-Inductively-Coupled Plasma-Mass Spectrometry (HPLC/DIN/ICP/MS).

One partnership involved collaborative work between Professor J. Bolton of the University of Western Ontario and the Dioxin Laboratory of LSB. No new analytical techniques were developed in this study - rather, reference centre services were provided to investigate the outputs of a specialized waste destruction system under development.

Another collaboration involved the Ministry of Health, Ministry of Environment and Energy, the University of Guelph, and the Ministry of Agriculture, Food & Rural Affairs to develop and evaluate improved methods for the detection of Cryptosporidium Oocysts in potable water. Such studies of a major public health issue benefit from a variety of sources applying new technology. The range of services provided in the partnerships described herein attest to the ongoing development of LSBs reference centre capabilities.

I. The Application of Quadrupole Ion Trap Mass Spectrometry to the Development of New Analytical Protocols for Dioxins and Furans

| | |
|---------------|---|
| Study Leader: | Professor Ray March (Trent University) |
| Partnership: | Roger Mercer (Laboratory Services Branch), Varian Associates (ERP 701G) |
| Customer: | Dioxin/Furan Unit |

Objectives

To discover the optimum operating conditions for analyzing dioxins and furans by ion trap mass spectrometry and to compare results with those found by using other mass spectrometry techniques.

Background

This work is a collaboration between Prof. Ray March of Trent University, Varian Associates, and LSB/DFU. A Saturn 4 ion trap on loan from Varian was located at LSB for one year, from July 94 to July 95. During this time the first set of results, described below, were produced. This work is to be published in *Analytical Chemistry*. The majority of the second set of results were also compiled at LSB. In July 95, the instrument was moved to Trent to allow Professor March and his research group to complete the remaining work.

Results

MS/MS conditions have been determined for maximum production of diagnostic fragment ions from selected precursor ions (i.e. optimal conversion efficiency) by using native dioxin/furan standard solutions. This study is complete and a publication based on the results has been accepted by *Analytical Chemistry*. Instrumental methods to analyze for both native and labelled ions in a single GC run and the determination of instrumental detection limits using standard solutions have also been completed. In addition, the linear working range and between-run variation in relative response

factors using standard solutions have been determined.

Current Status

The use of protracted ion storage times and/or unidirectional ion ejection to improve sensitivity is being studied at Trent University. The method detection limits for one or more of DFUs standard blank matrices using ion trap will also be determined at Trent. Joint work remaining between Trent and the Laboratory Services Branch involves the analysis of difficult field samples using ion trap MS/MS, and comparing the results with high resolution and triple quadrupole mass spectrometry.

II. Supercritical Fluid Extraction (SFE) of Soil Samples for Dioxins/Furans

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|---------------|---|
| Study Leader: | Dave Waddell (Laboratory Services Branch) |
| Partnership: | Eric Reiner (MOEE), Clayton Babcock (Dionex), Dave Herbert (ASL Ltd.) |
| Customer: | Analytical Laboratory Services |

Objective

To Determine whether SFE methods developed by ASL Laboratories are suitable for the determination of PCDDs/PCDFs in soil and sediment samples.

Background

A Dionex Model 723 Supercritical Fluid Extraction (SFE) unit, consisting of a 703 extractor and a 703M co-solvent addition module, was delivered to the Dioxin/Furan unit during February, 1995. The equipment had previously been used as a demonstration unit at Analytical Service Laboratories, Vancouver, B.C. and was

delivered to LSB on an "as is" basis. Preliminary results conducted at ASL showed some encouraging recoveries for sediment reference materials.

Results

Initial efforts at LSB focussed on repeating the results achieved by ASL using sediment reference materials. Following a brief training session by Dionex, sample cells were extracted and proven clean. A first attempt at evaluating recoveries from spiked samples was made using Ottawa sand spiked with 13C-labelled surrogates. Recoveries ranged from 15 to 50%. A further two sets of experiments using increased extraction times were unable to improve upon these recoveries. Thirty-four samples were generated during the entire course of the project.

Numerous instrumental operating problems were encountered, including leaking cells, blocked restrictors, and bent vent needles. In addition to these commonly experienced faults, a number of major setbacks were encountered that prevented the objectives of this study from being achieved.

Current Status

The transfer of technology from ASL to LSB was not successful. The equipment provided by Dionex was found to be prone to faults and required a high degree of operator intervention. Recoveries were found to be unacceptable for spiked samples. The SFE technique may be acceptable for the extraction of PCDDs/PCDFs from solid sample types, but this was not demonstrated.

III. Field Evaluation of a Membrane Filter/ Dissolution Method for the Recovery of Cryptosporidium Oocysts from Potable Water

| | |
|----------------|--|
| Study Leaders: | Gary Palmateer, Southwestern Region Michael Brodsky, Ministry of Health |
| Partnership: | Environmental Sciences & Standards Division (MOEE), Central and London Public Health Laboratories (MOH), University of Guelph (Environmental Biology Dept.), Ontario Ministry of Agriculture, Food & Rural Affairs. |
| Customers: | MOH Public Health Branch, MOEE EMRB |

Objectives

1. To establish the efficacy of the method using spiked water samples;
2. To determine the optimum filter media and sample volumes providing maximum oocyst recovery from drinking and surface waters;
3. To investigate the effectiveness of pre-filters when applied with high turbidity waters;
4. To establish official sampling and analysis methods for MOEE and MOH;
5. To develop and test a rugged, simple sampling cartridge for routine field use.

Background

The laboratories of the ministries of Environment & Energy (Laboratory Services Branch and Southwest Region Laboratory) and Health (Central and London Public Health Laboratories) are evaluating the efficacy of the method of recovery of Cryptosporidium oocysts from spiked potable waters. The method was recently developed by Drs Abdul Chagla and John Aldom of the London Public Health Laboratory (MOH) using in-house spiked water samples. The method is currently being adapted to field use and undergoing rigorous field testing at selected water plants in southwestern Ontario. Sampling is performed by MOEE staff with identification,

enumeration and confirmation of cryptosporidium oocysts by MOH laboratories.

Drs Hung Lee and Jack Trevors at the University of Guelph and Dr. Stephanie DeGrandis (OMAFRA) are cooperating on a research project on advanced methods of detection, enumeration, confirmation and viability assessment using polymerase chain reaction (PCR) technology, under a grant provided by MOEE and OMAFRA.

Results

Initial experiments established that the required sample volumes of 800-1000 litres of spiked treated drinking water may be filtered using a 29.3 cm diameter cellose acetate filter of 1.2 um pore size. This filter media was modified to a nominal 8 um pore size as a result of plugging of the 1.2 um filter with samples demonstrating high turbidity. Filters contain the oocysts are dissolved in acetone, centrifuged, the acetone decanted, the oocysts washed in water/ ethanol and submitted for staining and microscopic examination. Percent recoveries using the original 1.2 um filter varied widely (8.5 - 130%, average 45.6%) but improved and stabilized with the 8 um filter (60 - 90%, average nn%). This represents a major performance improvement compared to the USEPA/ASTM method and the sampling and testing can be accomplished within 2 days.

Current Status

The 8 um pore size cellulose acetate filter appears to be working very dependably. Work is progressing to develop a standard sampling cartridge to house the filter and make it more practical. The method has been successfully applied to sample drinking water during a recent outbreak of cryptosporidiosis in Collingwood Ontario. Work continues to document the method as the official method of both MOEE and MOH.

IV. Accelerated Solvent Extraction (ASE) of Soil Samples for Dioxins/Furans

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|---------------|---|
| Study Leader: | Dave Waddell (Laboratory Services Branch) |
| Partnership: | David Knowles (Dionex Corporation) |

Objective

To determine whether accelerated solvent extraction (ASE) methods are suitable for the determination of PCDDs and PCDFs in soil and sediment samples.

Background

The ASE technique uses conventional liquid solvents at elevated pressures and temperatures. Under these conditions, the kinetic processes for the desorption of analytes from the matrix are accelerated. Extraction times and solvent volumes are dramatically reduced as compared to classical extraction techniques, such as Soxhlet.

Well-characterized sediment samples were obtained from the National Water Research Institute and the National Research Council Institute for Marine Biosciences. Both samples are being investigated as candidate standard reference materials and consensus values for PCDD/Fs are available from round robin studies. The samples were extracted using ASE at the Salt Lake City Technical Centre of Dionex Corporation and later cleaned-up and analyzed for PCDD/Fs by the Dioxin/Furan Unit at LSB. Data were compared to results obtained using Soxhlet extraction.

Results

Some discrepancies were found to exist when comparing the extraction results by using Soxhlet and by using the ASE - principally with the PCDD/F group totals. Sample inhomogeneity could not be ruled out as a possible contributing factor. However, the correspondence of the 2,3,7,8-substituted PCDD/F congeners was found to be excellent. Surrogate recoveries for the entire data set were 78% via Soxhlet and 70% using ASE for a high concentration sample and 56% and 66%, respectively, for a

low concentration sample.

The data suggest that results obtained by using the ASE technique are essentially equivalent to those obtained by using established MOEE Soxhlet-based methods. As ASE extractions may be performed in less time (~ 15 minutes) and with less solvent (~20 ml) compared to Soxhlet extractions, ASE appears to be a superior extraction technique. The only disadvantage to ASE is the high initial cost of the apparatus.

V. UV Photolysis of Pentachlorophenol

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|---------------|--|
| Study Leader: | Professor J. Bolton (University of Western Ontario) |
| Partnership: | Dave Waddell (Laboratory Services Branch), Solarchem |

Objective

To evaluate the destructive potential of UV photolysis for the treatment of pentachlorophenol (PCP) contaminated wastewaters.

Background

The degradation and destruction of wastewaters contaminated with organic pollutants may routinely be accomplished using ultraviolet (UV) light. The most common technology involves the addition of hydrogen peroxide followed by irradiation with powerful (up to 30 kW) UV lamps. Highly reactive hydroxyl radicals are generated from the hydrogen peroxide under UV conditions, enhancing the rate of oxidation relative to direct photolysis. Such processes are known as advanced oxidation processes (AOPs). The use of AOPs for the treatment of PCP-contaminated waters has come under scrutiny owing to the possibility of producing intermediates which are far more toxic than is PCP. In particular, the formation of PCDD/F's is of great concern. In the current work, the destruction of analytical grade PCP was monitored following UV irradiation in a laboratory scale reactor equipped with a medium pressure 1 kW lamp.

Results

Initial experiments were conducted using direct photolysis and photolysis in the presence of hydrogen peroxide. The PCP destruction and PCDD/F formation was monitored over 12 and 6 minutes, respectively, for the two sets of conditions. Gradually increasing levels of PCDD/Fs were observed with increasing time, with the highest levels (137 ppq TEQ's) being observed for the direct photolysis samples over 12 minutes. At times beyond 2 hours, the levels of PCDD/Fs maximized at 32 minutes and then declined steadily. The addition of catalyst in the presence of hydrogen peroxide was found to greatly reduce the levels of PCDD/Fs. Under these conditions, all photolysate samples were found to contain \leq 26 ppq of TEQ's, are below the regulatory limit for discharge of industrial effluents under MISA guidelines.

Current Status

The last set of dioxin samples for this study have been processed. The data confirm that use of a catalyst in addition to the UV photolysis enhances dioxin destruction. No additional dioxin analyses are planned, and a journal publication of this work is in preparation.

VI. Speciation of Aluminum in Drinking Water by HPLC/DIN/ICP/MS

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|---------------|--|
| Study Leader: | Mark Powell |
| Partnership: | Daniel Wiederin (Cetac Technologies) |
| Customer: | Wastewater Technology Section (Heather Broomer), Standards Development Branch |

Objective

To investigate the complex chemistry of aluminum to find a relationship between soluble and insoluble aluminum species and to develop a method to measure "free" ionic aluminum.

Background

Presently, there are concerns with negative human health effects from aluminum in drinking water. Although there are many conflicting reports in the literature, measurement of "free residual" aluminum has been requested in addition to the established method for "total" aluminum determination. The customer has established a desire to find a relationship between soluble and insoluble aluminum under different water quality conditions (ie; pH, alkalinity, TOC, etc.).

An analytical technique based on separation by ion chromatography using a micro-column developed by Cetac Technologies and designed for ionic speciation of aluminum is being investigated. As the detection system used is DIN/ICP/MS, the technique is selective and sensitive enough to monitor total ionic and speciated ionic aluminum at concentrations below typical drinking water levels.

Results

Initial results indicate that an ionic aluminum chromatogram can be produced from the micro-column. Total aluminum was also determined in the same measurement. The retention time of the signal is consistent - leading to a possibility of quantitative measurements. The detection limit is currently estimated to be in the ppb range.

Current Status

Column characterization still has to be performed to achieve optimum performance characteristics to resolve peaks for individual species. There is an unknown peak that has to be yet identified. A relationship between sample stability must be investigated as well as possible interferences to the column from drinking water matrices. Neutral or anionic species (AlF_3 , or AlF_4^+) also exist in the soluble portion of the sample. These species should be investigated by alternate means such as tandem columns.

Publications and Presentations - 1995

Analytical Laboratory Services

A. Publications

1. J.B. Plomley, R.S. Mercer, and R.E. March. Optimization of the Quadrupole Ion Storage Mass Spectrometer for the Tandem Mass Spectrometric Analysis of Dioxins and Furans. *Organohalogen Compounds 1995*, 23, 7-12.
2. David E. Knowles, Bruce E. Richter, John Ezzell, Frank Höfler, David S. Waddell, Tereza Gobran, and Vin Khurana. Extraction of Chlorinated Compounds by Accelerated Solvent Extraction (ASE). *Organohalogen Compounds 1995*, 23, 13-18.
3. Karen A. MacPherson, Eric J. Reiner, David S. Waddell, and Kathy Z. Taylor. A Comparison of Relative Response Factors for Polychlorinated Dibenzo-p-dioxins and Dibenzofurans Using Triple Quadrupole and High Resolution Mass Spectrometry. *Organohalogen Compounds 1995*, 23, 99-104.
4. Lisa Wong Rerup, Terry Kolic, Vin Khurana, Karen MacPherson, Kathy Taylor, and Dave Waddell. Supercritical Fluid Extraction of Soil Samples for the Analysis of PCDDs and PCDFs Using Isotope Dilution Quantitation. *Organohalogen Compounds 1995*, 23, 145-149.
5. Ray E. Clement. Data Quality Issues for Ultra Low-Level PCDD/PCDF Data Analysis. *Organohalogen Compounds 1995*, 23, 283-285.
6. David S. Waddell, Hanna Bonek-Ocieszko, and Tereza Gobran. PCDD/PCDF Formation by UV Photolysis of Pentachlorophenol With and Without the Addition of Hydrogen Peroxide. *Organohalogen Compounds 1995*, 23, 407-412.
7. E.J. Reiner, W.I. Gizyn, V. Khurana, T.M. Kolic, K.A. MacPherson, D.S. Waddell, R.W. Bell, and R.J. Schreiber, Jr. Environmental Impact of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans from a Cement Kiln. *Organohalogen Compounds 1995*, 23, 419-423.

8. Tereza Gobran, Vin Khurana, Karen MacPherson, and Dave Waddell. PCDD/PCDF Levels in Raw Sewage, Final Effluent, Sludge, and Ash Samples from an Ontario Waste Water Treatment Plant. *Organohalogen Compounds* 1995, 24, 75-80.
9. T.M. Kolic, K.A. MacPherson, E.J. Reiner, and W.D. McIlveen. Norwegian Spruce Needles: A Monitoring Technique for PCDD/Fs During and After a Tire Fire. *Organohalogen Compounds* 1995, 24, 195-200.
10. Eva Duchoslav, Dan Orr, and Ray Clement. Concentrations and TEQs of PCDD/PCDF in Urban and Rural Precipitation. *Organohalogen Compounds* 1995, 24, 201-204.
11. E.J. Reiner, K.A. MacPherson, T.M. Kolic, A. Hayton, and R.E. Clement. Characteristic Levels of Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Fish From Ontario Great Lakes. *Organohalogen Compounds* 1995, 24, 379-384.
12. R.E. Clement, G.A. Eiceman, and C. Koester. Environmental Analysis. *Anal. Chem.* 1995, 67, 221R-255R.
13. R.E. Clement and C.J. Koester. Quality Control and Quality Assurance Aspects of Gas Chromatography-Mass Spectrometry for Environmental Analysis. Chapter 6 in Quality Assurance for Environmental Monitoring: Instrumental Methods; G. Subramanian, Ed., VCH Publishers, Weinheim, Germany 1995, 193-211.
14. P.J. Steer, C.H.M. Tashiro, W.D. McIlveen, and R.E. Clement. PCDD and PCDF in Air, Soil, Vegetation and Oily Runoff from a Tire Fire. *Water, Air and Soil Pollution* 1995, 82, 659-674.
15. K.Z. Taylor, D.S. Waddell, E.J. Reiner, and K.A. MacPherson. Direct Elution of Solid Phase Extraction Disks for the Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in Effluent Samples. *Anal. Chem.* 1995, 67, 1186.
16. M.J. Powell, D.W. Boomer, and D.R. Wiederin. Determination of Chromium Species in Environmental Samples Using HPLC-DIN-ICP-MS. *Anal. Chem.* 1995, 67, 2474-2478.

17. S. Luek Wong, L. Nakamoto, and J.F. Wainwright. Detection and Toxicity of Titanium from Pulp and Paper Effluents. *Bull. Environ. Contamin. Toxicol.* **1995**, *55*, 878-885.
18. Joan Crowther, Francis B. Lo, Michael W. Rawlings, and Bernard Wright. Determination of Organically Bound Sulfur in Swamp and Terrestrial Waters by Continuous Flow Oxidation and Ion Chromatography. *Environ. Sci. Technol.* **1995**, *29*, 849-855.
19. S. Luek Wong, J.F. Wainwright, and L. Nakamoto. Monitoring Toxicity in Four Wastewaters in the Bay of Quinte, Lake Ontario. *J. Great Lakes Res.* **1995**, *21*, 340-352.
20. V. Kanagasabapathy, R. Bell, P. Yang, L. Allan, L. Au, J. Parmar, M. Lusis, and R. Chapman. Development in the Supercritical Fluid Extraction of PAHs from Environmental Matrix. *Chrom. Sci.* **1995**, *33*, 467.
21. Ray Clement. How Much is There? A Classroom Experiment in Measurement Science. *Interactions* **1995**, *7*(4), 24-27.
22. Ray E. Clement. "Dioxins and Furans" in: *Conservation and Environmentalism: An Encyclopedia*, Robert Paehlke, ed.; Garland Publishing Inc., New York **1995**, 176-177.
23. Ray E. Clement. "Love Canal" in: *Conservation and Environmentalism: An Encyclopedia*, Robert Paehlke, ed.; Garland Publishing Inc., New York **1995**, 417-418.
24. Ray E. Clement. "Toxic Pollutants, Transport and Fate" in: *Conservation and Environmentalism: An Encyclopedia*, Robert Paehlke, ed.; Garland Publishing Inc., New York **1995**, 630.
25. Ray E. Clement. "Trace Analysis" in: *Conservation and Environmentalism: An Encyclopedia*, Robert Paehlke, ed.; Garland Publishing Inc., New York **1995**, 634-635.
26. Stephen W.D. Jenkins, Carolyn J. Koester, Vincent Y. Taguchi, David T. Wang, Jean-Paul Palmentier, and Kim P. Hong. N-Nitrosodimethylamine in Drinking Water Using a Rapid, Solid-Phase Extraction Method. *Environ. Sci. & Pollut. Res.* **1995**, *2*(4), 207-210.

27. Ray Clement and Eric J. Reiner. The Evolving Field of Ultra-Trace Analysis (dioxin analysis past, present, and future). *The Standard 1995*, 2(1), Newsletter of *Cambridge Isotope Laboratories*, Andover, Massachusetts.
28. Ray Clement. Science at Your Service. *The Crucible 1995*, 26(5), 31-34.

B. Presentations

1. *R.E. Clement*, "Key Employment Skills"; Invited Lecture, Fanshawe College, December 8, 1995, London, Ontario.
2. *R.E. Clement*, "Environmental Careers in the Laboratory Testing Industry: Past, Present, Future"; Presented at A&WMA Student Chapter 'Career Night', University of Guelph, November 28, 1995, Guelph, Ontario.
3. *R.E. Clement*, "Analytical Chemistry in the Real World"; Presented to 2nd Year Undergraduate Class, University of Waterloo, November 22, 1995, Waterloo, Ontario.
4. *R.E. Clement*, "Graduate Environmental Education: Ministry of Environment and Energy - One Perspective"; Presented at the Workshop on Interdisciplinary Graduate Programs in Environmental Sciences, November 10, 1995, The University of Western Ontario, London, Ontario.
5. *R.E. Clement*, "How to Write a Proposal"; Seminar Presented to Undergraduate Students, McMaster University, October 3, 1995, Hamilton, Ontario.
6. *R.E. Clement*, "Data Quality Issues for Ultra Low-Level PCDD/PCDF Data Analysis"; Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 24, 1995, Edmonton, Alberta.
7. E.J. Reiner, K.A. MacPherson, T.M. Kolic, A. Hayton, *R.E. Clement*, "Characteristic Levels of Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Fish from Ontario Great Lakes"; Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 23, 1995, Edmonton, Alberta.

8. *E. Duchoslav*, D. Orr, R.E. Clement, "Concentrations and TEQs of PCDD/PCDF in Urban and Rural Precipitation"; Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 23, 1995, Edmonton, Alberta.
9. *R.E. Clement*, "The Scientist in Modern Society: Facts, Myths, and Ethics"; Talk Presented at KEY Society Meeting, Sarnia, Ontario, July 26, 1995.
10. *R.E. Clement*, "Environmental Education: Essential Contributions from Government and Industry"; Invited Paper Presented at the 78th Annual Canadian Society for Chemistry Conference, Guelph, Ontario, May 31, 1995.
11. *R.E. Clement*, "Job Opportunities in Analytical Chemistry"; Talk Presented to Centennial College Students, Laboratory Services Branch, Etobicoke, March 20, 1995.
12. *R.E. Clement*, "Part per Quadrillion Dioxin Determinations: Real or Imaginary?"; Invited Lecture Presented at *Varian Day*, Carleton University, April 10, 1995.
13. *R.E. Clement*, "Methods for Ultra-Trace Organic Compound Determinations"; Invited Lecture Presented to 3rd year students, Erindale College, April 3, 1995.
14. *J.B. Plomley*, R.S. Mercer, and R.E. March. Optimization of the Quadrupole Ion Storage Mass Spectrometer for the Tandem Mass Spectrometric Analysis of Dioxins and Furans. Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 21-25, 1995, Edmonton, Alberta.
15. *David E. Knowles*, Bruce E. Richter, John Ezzell, Frank Höfler, David S. Waddell, Tereza Gobran, and Vin Khurana. Extraction of Chlorinated Compounds by Accelerated Solvent Extraction (ASE). Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 21-25, 1995, Edmonton, Alberta.
16. Karen A. MacPherson, *Eric J. Reiner*, David S. Waddell, and Kathy Z. Taylor. A Comparison of Relative Response Factors for Polychlorinated Dibenzo-p-dioxins and Dibenzofurans Using Triple Quadrupole and High Resolution Mass Spectrometry. Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 21-25, 1995, Edmonton, Alberta.

17. Lisa Wong Rerup, Terry Kolic, Vin Khurana, Karen MacPherson, Kathy Taylor, and *Dave Waddell*. Supercritical Fluid Extraction of Soil Samples for the Analysis of PCDDs and PCDFs Using Isotope Dilution Quantitation. Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 21-25, 1995, Edmonton, Alberta.
18. *David S. Waddell*, Hanna Bonek-Ocieszko, and Tereza Gobran. PCDD/PCDF Formation by UV Photolysis of Pentachlorophenol With and Without the Addition of Hydrogen Peroxide. Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 21-25, 1995, Edmonton, Alberta.
19. *E.J. Reiner*, W.I. Gizyn, V. Khurana, T.M. Kolic, K.A. MacPherson, D.S. Waddell, R.W. Bell, and R.J. Schreiber, Jr. Environmental Impact of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans from a Cement Kiln. Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 21-25, 1995, Edmonton, Alberta.
20. Tereza Gobran, Vin Khurana, Karen MacPherson, and *Dave Waddell*. PCDD/PCDF Levels in Raw Sewage, Final Effluent, Sludge, and Ash Samples from an Ontario Waste Water Treatment Plant. Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 21-25, 1995, Edmonton, Alberta.
21. T.M. Kolic, K.A. MacPherson, *E.J. Reiner*, and W.D. McIlveen. Norwegian Spruce Needles: A Monitoring Technique for PCDD/Fs During and After a Tire Fire. Presented at the 15th International Symposium on Chlorinated Dioxins and Related Compounds, August 21-25, 1995, Edmonton, Alberta.
22. *J.B. Plomley*, R.S. Mercer, and R.E. March. Optimal Ion Trap MS/MS Parameters for the Analysis of Dioxins and Furans. Presented at the 43rd ASMS Conference on Mass Spectrometry and Allied Topics, Atlanta, Georgia, May, 1995.

23. *Roger S. Mercer, Jeffery B. Plomley, Jennifer A. Townsend, Dave S. Waddell, and Raymond E. March.* Dioxin and Furan Analysis by Ion Trap, Triple Quadrupole MS/MS, and HRMS. Presented at the 43rd ASMS Conference on Mass Spectrometry and Allied Topics, Atlanta, Georgia, May 25, 1995.
24. *V.Y. Taguchi, C.J. Koester, and K.-P. Hong.* LC/MS in Environmental Samples. Presented at the Spectroscopy Society of Canada 6th Annual Symposium: *Advances in Analytical Chemistry*, April 1995, Toronto, Ontario.
25. *Patrick Crozier.* Protecting Ontario's Drinking Water - An Analytical Perspective. Award Lecture Presented at the Government of Ontario Analytical Laboratory Council (GOALS) Fall Meeting, October 19, 1995, Toronto, Ontario.

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